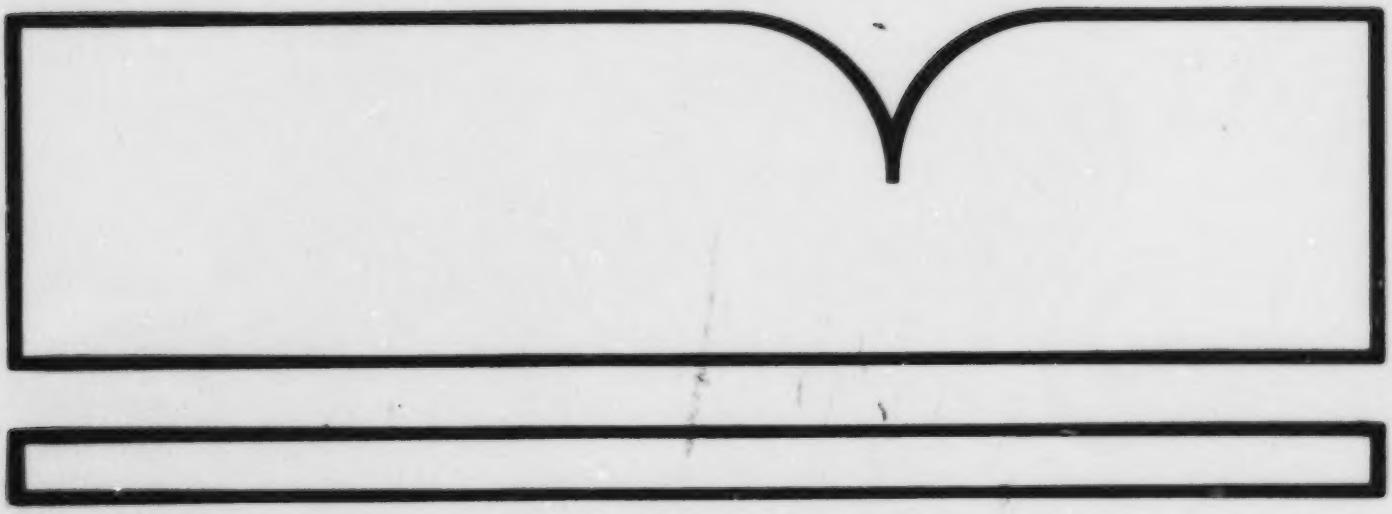
PB84-177930

Atmospheric Volatile Hydrocarbon Composition at Five Remote Sites in Northwestern North Carolina

(U.S.) Environmental Sciences Research Lab.
Research Triangle Park, NC

Apr 84



U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-177930

EPA-600/D-84-092
April 1984

ATMOSPHERIC VOLATILE HYDROCARBON COMPOSITION AT FIVE REMOTE SITES IN NORTHWESTERN NORTH CAROLINA

by

Robert L. Seila and Robert R. Arnts
Environmental Sciences Research Laboratory
Research Triangle Park, NC 27711

and

James W. Buchanan
Appalachian State University
Boone, NC

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/D-84-092		PB84 187930

4. TITLE AND SUBTITLE	5. REPORT DATE
ATMOSPHERIC VOLATILE HYDROCARBON COMPOSITION AT FIVE REMOTE SITES IN NORTHWESTERN NORTH CAROLINA	1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Robert L. Seila, Robert R. Arnts, and James W. Buchanan	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	CDWA1A-02 Task 4034
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	14. SPONSORING AGENCY CODE EPA 600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

The results of a study to measure the volatile hydrocarbon composition of the atmosphere at several sites in the southern Appalachian Mountains of northwestern North Carolina are presented. Ambient air was sampled repeatedly at five geographically and botanically different remote sites from September 1981 to October 1982. In addition, limited sampling was done in and just outside the town of Boone, NC. Samples were collected in stainless steel canisters and analyzed for C-2 to C-12 hydrocarbons by gas chromatography with flame ionization detection. The nonmethane total hydrocarbon concentrations at the remote sites ranged from 32 to 132 ppbC. The range of identified paraffins, olefins, and aromatics concentrations was 7 to 65 ppbC, 1 to 8 ppbC, and 2 to 20 ppbC, respectively. Isoprene and α-pinene made up a small portion of NMTHC, ranging from less than 0.05 to 13 ppbC and less than 0.05 to 9 ppbC, respectively. Unknown peaks eluting mostly in the post-C-9 region of the chromatogram were a significant portion of the NMTHC, ranging from 13 to 108 ppbC. The identity and source of the unknown compounds are not well understood, although some of them are probably biogenic. Isoprene and α-pinene displayed a distinct seasonal variation related to ambient temperature; whereas, acetylene and the sum of paraffins, olefins, and aromatics showed no seasonal variation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	28
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ATMOSPHERIC VOLATILE HYDROCARBON COMPOSITION AT FIVE REMOTE SITES IN NORTHWESTERN NORTH CAROLINA

Robert L. Seila

Robert R. Arnts, Environmental Sciences Research Laboratory
U.S. EPA, Research Triangle Park, NC and
James W. Buchanan, Appalachian State University, Boone, NC

The results of a study to measure the volatile hydrocarbon composition of the atmosphere at several sites in the southern Appalachian Mountains of northwestern North Carolina are presented. Ambient air was sampled repeatedly at five geographically and botanically different remote sites from September 1981 to October 1982. In addition, limited sampling was done in and just outside the town of Boone, NC. Samples were collected in stainless steel canisters and analyzed for C-2 to C-12 hydrocarbons by gas chromatography with flame ionization detection. The nonmethane total hydrocarbon concentrations at the remote sites ranged from 32 to 132 ppbC. The range of identified paraffins, olefins, and aromatics concentrations was 7 to 65 ppbC, 1 to 8 ppbC, and 2 to 20 ppbC, respectively. Isoprene and α-pinene made up a small portion of NMTHC, ranging from less than 0.05 to 13 ppbC and less than 0.05 to 9 ppbC, respectively. Unknown peaks eluting mostly in the post-C-9 region of the chromatogram were a significant portion of the NMTHC, ranging from 13 to 108 ppbC. The identity and source of the unknown compounds are not well understood, although some of them are probably biogenic. Isoprene and α-pinene displayed a distinct seasonal variation related to ambient temperature; whereas, acetylene and the sum of paraffins, olefins, and aromatics showed no seasonal variation.

ATMOSPHERIC VOLATILE HYDROCARBON COMPOSITION AT FIVE REMOTE SITES IN NORTHWESTERN NORTH CAROLINA

Introduction

Since the work of Went (1-2) and Rasmussen (3) in the 1960's considerable debate has arisen about the role of biogenic hydrocarbons in the production of photochemical oxidants and in the formation of "blue haze" in vegetated areas. Many investigations have been performed to determine emission rates of terpenes and other natural hydrocarbons, to study their photochemistry, and to determine their concentrations in ambient air. Several reports reviewing and analyzing this research have been written (4-8). Many authors on this issue have suggested that more information on the ambient air concentrations of biogenic hydrocarbons and their contribution to nonmethane total hydrocarbon (NMTHC) concentration is needed.

Previous research has shown that although terpenes are the bulk of biogenic hydrocarbons, other hydrocarbons are also emitted from vegetation (9). Since the source of the "other hydrocarbons" is very difficult to determine the investigation of ambient air concentrations of biogenic hydrocarbons has focused on those terpenes that can be separated and detected on a gas chromatographic (gc) column. The concentrations of these terpenes—primarily isoprene, α-pinene, β-pinene, limonene, myrcene, and 3-carene (7)—are reported to be low in absolute concentration, usually in the low ppbC range, and low as a contribution to NMTHC, usually less than 10% (10).

Hydrocarbon concentrations at remote sites in the southern Appalachian Mountains, which is the subject of this paper, have been determined previously by three investigative groups. In 1975-76, Ferman (11) measured hydrocarbons at four rural sites in or near the southern Applachian Mountains: one in western North Carolina, one in central Kentucky, and two in south-central Virginia. He compares typical concentrations for alkanes, alkenes, isoprene, terpenes, C-6 to C-8 aromatics and formaldehyde for rural and urban sites. In September 1978 separate groups of investigators from Washington State University (WSU) and the U.S. Environmental Protection Agency (EPA) collected and analyzed samples in the Great Smoky Mountains National Park. Their studies lasted only one week, with 12 samples being analyzed by WSU (12) and 9 by EPA (10).

In this paper, we report the results of detailed hydrocarbon analyses of 53 ambient air samples collected over a period of 13 months at five remote and two urban locations in the mountains of northwestern North Carolina. We compare our results to those of the investigators previously cited.

Experimental Methods

Sampling

Air samples were collected in 4.5-L stainless steel canisters fitted with two brass valves (Nupro Company, Cleveland, OH). The canisters

were internally electropolished by the Summa process (Molectric Inc., Englewood, CA). Before transport to a field location, the canisters were flushed with helium and evacuated by a mechanical forepump. A liquid nitrogen cooled trap was located between the forepump and canister to prevent hydrocarbon contamination from the pump oil. Twenty ml of a 50 ppm NO in N_2 mixture were added to the canisters to destroy ambient ozone that could react with olefinic hydrocarbons during storage in the canisters.

At the sampling sites, canisters were opened to the atmosphere, then pressurized to 170 kPa by means of a Teflon-lined diaphragm, 12-V dc pump (Thomas Industries, Sheboygan, WI). The pump was powered by a 12-V heavy duty storage battery (Deka T27 Deep Cycle, East Penn Mfg, Lyon Station, PA). Canister pressure was measured with an aneroid gauge. Canisters were mailed as soon after collection as possible to the U.S. Environmental Protection Agency, Research Triangle Park, NC, for analysis. Periodically duplicate samples of air were taken, using a T-connection from the pump to the canisters.

Ozone measurements were made with a portable, battery-powered, ozone-ethylene chemiluminescence meter calibrated with an ozone generator. Calibrations were done once a month, and the generator output was verified with a UV spectophotometer. Nitrogen dioxide measurements were also made using a modified Saltzman bubbling technique (19). Bubbling was carried out for 24 hr, using a portable single impinger bubbler unit powered by a 6-V battery.

Site Descriptions

Five distinctively different geographical and botanical areas were sampled repeatedly between September 1981 and October 1982. All sites were located in the southern Appalachian Mountains of northwestern North Carolina. In addition, limited sampling was conducted within and just outside the town limits of Boone, NC.

Linville Gorge. This site is an officially designated federal wilderness area. No motorized traffic is allowed near the Linville River proper, although unpaved roads allow access to the rim of the gorge. Elevations of upper and lower sampling sites were approximately 1,220 and 910 m. The lower site was at river's edge, the upper just removed from an unpaved access road of very low traffic density (one vehicle per hour or less on a typical weekday). No urban areas exist in the immediate vicinity.

Grandfather Mountain. All sampling was done at two heavily wooded sites well away (3000 m or more) from the Visitor's Center and Swinging Bridge area, which attract heavy tourist traffic during a large part of the year. The lower site is within 400 m of a heavily traveled highway, but is several hundred feet higher in elevation than the highway. Elevation of lower and upper sites were 1340 and 1740 m, respectively. The upper site was on a little-used hiker's trail quite remote from traffic or other human disturbances.

Roan Mountain. Three sampling sites were all situated at approximately 1,800 m elevation, on or near the Appalachian Trail section extending from Carver's Gap roadhead to Big Yellow Mountain. The lower site was in dense Fraser fir, near (within 100 m) a paved road of low (10 vehicles per hour) traffic density. The two upper (more remote) sites were on a highly exposed bald (high grasses, low alder bush and heaths) and just down from the bald in a hardwood forest. No urban areas exist nearby, and these sites are probably geographically the most remote sampled during the study.

Deer Park. This area lies near the Blue Ridge Parkway, about 3200 m from the town of Blowing Rock, NC (population 1,000 yearround residents). This is a resort area both summer and winter, but there is no heavy industry nearby. A lower sampling site is roughly 400 m from Shulls Mill Road, which is a lightly traveled (50 cars per hour) paved road adjoining the Parkway. An upper site is quite remote, with no access roads and very light hiker traffic on trails. Elevations of the sites were 1070 and 1370 m respectively.

Boone Fire Tower. The fire tower is on Rich Mountain about 2400 m northwest of the center of Boone, NC (population 10,000). Boone is a university town with very little industry. The tower, located for optimal viewing in all directions, has high exposure to prevailing northerly winds that have not yet reached the Boone-Blowing Rock area. Samples were taken at the base and at the top of the 23-m tower.

Downtown Boone and Boone Outskirts. During the latter phase of the sampling period, several canisters were taken near the center of Boone proper. The university steam plant (coal and oil fired) and several fast-food restaurants were in the immediate vicinity. Samples on the outskirts of Boone were taken 1500 to 3000 m downwind, from the same air parcel (as estimated from wind speed and direction).

Hydrocarbon Determination

Hydrocarbons were determined by gas chromatography and flame ionization detection (GC-FID). The C-2 to C-4 hydrocarbons were separated on a 1.8-m by 0.32-cm-ID stainless steel column packed with 80-100 mesh, grade 58 silica gel. Column temperature was programmed from 50°C, held for 2 min, to 100°C at 8°C/min. The C-4 to C-12 hydrocarbons were separated on a 60-m, 0.32-mm-ID fused silica capillary column (J&W Scientific) with a 0.5-μm-thick film of DB-1 bonded liquid phase. Temperature was programmed from -50°C, held for 1 min, to 120°C at 8°C/min, and held at 120°C for 5 min. For both analyses, 450 ml of sample air were cryogenically preconcentrated using a procedure described elsewhere (13). The limit of detection for both analyses was less than 0.05 part-per-billion carbon (ppbC). Mean precision and accuracy were estimated to be ±3% (coefficient of variation) and ±10% (95% confidence interval) respectively. A 2.74 ppm propane-in-air standard reference material from the National Bureau of Standards was the calibration gas. Individual compounds were identified by retention time.

Results and Discussion

A statistical summary listing the median, minimum, and maximum concentration for 46 individual hydrocarbons or groups of hydrocarbons for the seven sampling locations is given in the appendix.

Table I presents the median concentrations, percentage composition, and number of samples for each of the seven locations for the compound categories of acetylene, paraffins, olefins, aromatics, biogenic HC, unknowns, and NMTHC. The data in this table are summations of median concentrations presented in the appendix. We used a summation of medians procedure, because for some of the samples contamination from an ethylene ozone analyzer and propane contamination from camp stoves would have eliminated many of the samples from the NMTHC calculation, although all of the other individual compound concentrations were good data. This method employs more of the data and produces a more accurate measure of central tendency than a determination of the medians from the compound category summations for each sample.

The NMTHC concentrations for the five remote sites ranged from a low of 32 ppbC at Roan Mountain to a high of 132 ppbC at Linville Gorge. The NMTHC results from Roan Mountain confirm that it was the most remote location. The median concentration at Roan Mountaiin, 40 ppbC, was very low. It was much lower than at the other four remote sites, and it was lower than the 87 ppbC minimum value reported by Arnts and Meeks (10) for the Smoky Mountains. Their median was 109 ppbC. The median NMTHC concentration for the 12 Smoky Mountain samples analyzed by Cronn and Harsch (12) was 86 ppbC. Our median NMTHC values for the other four remote sites were a little lower than the Cronn and Harsch (12) results, ranging from 68 to 85 ppbC. Table I shows that much higher NMTHC values were observed in the center and outskirts of Boone.

Paraffins were a significant portion of NMTHC ranging from 27% at Linville Gorge to 39% at Grandfather Mountain. The vast majority of the paraffin component was the C-2 to C-5 paraffins. The median concentration range was from a low 12 ppbC at Roan Mountain to 31 ppbC at Grandfather Mountain. The percent paraffins observed by Arnts and Meeks (10) was slightly higher, ranging from 37 to 47%. Their concentrations of paraffins were substantially higher, ranging from 35 to 76 ppbC. Ferman (11) and Cronn and Harsch (12) do not report complete paraffin composition. They only report light paraffin data which are not directly comparable to our data. We observed much higher paraffin concentrations in Boone center, but only about 20 ppbC higher and representing the same proportion of NMTHC as the remote locations, in Boone outskirts.

Median identified aromatics concentrations at the remote sites ranged from 3.4 ppbC at Roan Mountain to 6.5 ppbC at Grandfather Mountain. Benzene, toluene, ethylbenzene and m,p,o-xylene accounted for almost all of the aromatics component. Aromatics levels were considerably higher at Boone, 72 ppbC, and Boone outskirts, 16 ppbC. Arnts and Meeks (10) report a range of aromatics from 11 to 33 ppbC with a median of 20 ppbC for the Smoky Mountains. Ferman (11) reports that typical C-6 to C-8 aromatics concentrations in rural areas are approximately 2 ppbC. Our lowest concentration at Roan Mountain was 2.1 ppbC. Cronn and Harsch (12) only report toluene and do not report a sum of aromatics for their Smoky Mountain samples.

Median olefin concentrations at the remote sites were very low, ranging from 1.7 ppbC at Rich Mountain to 4.5 ppbc at Grandfather Mountain. Most of the olefins routinely measured in urban or suburban air were not detected in the remote samples. The olefin content was essentially ethylene and propylene. Arnts and Meeks (10) report Smoky Mountains olefin values ranging from 5.6 to 23.7 ppbC with a median of 12.0 ppbC. Ferman (11) reports that the typical concentration of C-2 to C-4 alkenes in rural areas is 1 ppbC. Cronn and Harsch (12) do not provide a sum of olefins for their Smoky Mountain data.

The median olefin concentration in Boone center was 12 to 32 times that of the remote sites, while the paraffin concentration was only 7 to 17 times higher, aromatics 11 to 21 times higher, and acetylene 5.7 times higher. These differences suggest that the air transported to the remote sites has undergone photochemical reactions with loss rates of olefins being highest followed by loss of aromatics, paraffins, and acetylene. Nelson and Quigley (14) have reported the use of the m,p-xylene:ethylbenzene ratio to estimate hydrocarbon age in ambient air. Because of the differential reaction rates of m,p-xylene, and ethylbenzene with hydroxyl radicals, the ratio decreases over time under conditions of sunlight irradiation. The ratio for both Boone center and Boone outskirts was 3.3 (Table I). The ratio decreased to 2 for all of the remote sites. Using Nelson and Quigley's figure 1 (14)(a plot of the variation of the m,p-xylene:ethylbenzene ratio with time for two smog chamber experiments), we estimate an average age for the anthropogenically emitted hydrocarbons at the remote sites of 3 to 4 hours.

Acetylene has been used by other investigators as a tracer of automobile exhaust and anthropogenic emissions, because it is produced in combustion processes and is quite stable in the atmosphere (16-17). Our median acetylene values were very low, ranging from 0.8 to 1.0 ppbC at the remote sites. Arnts and Meeks' (10) acetylene concentrations ranged from 2.5 to 7.5 ppbC. Cronn and Harsch's (12) values were very similar, ranging from 2.9 to 10.5 ppbC. Ferman's (11) average acetylene concentration at Keysville, VA, was 0.9 ppbC, which he states is typical of rural sites.

The largest component of NMTHC was the unknown hydrocarbon component (Table I). Unknowns at the remote sites ranged widely from 13 ppbC at Roan Mountain to 108 ppbC at Linville Gorge; however, as a percentage of NMTHC, their range was narrow, from 45 to 59%. The Boone outskirts' unknowns percentage, 45%, was similar to the remote locations, while the composition at Boone center was considerably lower at 22%. The unknowns reported by Cronn and Harsch (12) and Arnts and Meeks (10) for their Smoky Mountain samples were also quite high with median values of 36% and 24% respectively. Altshuller (8) points out that other investigators measuring hydrocarbons in rural areas report high compositions of unidentified hydroccarbons, ranging from 10 to 50%.

The biogenic hydrocarbons reported by us are isoprene and α-pinene. Other terpenes were not included, because we did not have confidence in our separation and retention time identifications. Several times samples were collected on Tenax cartridges for gas chromatographic-mass spectrometric (GC/MS) analysis; however, problems with the mass spectrometer prevented any GC/MS analyses from being completed.

Concentrations of isoprene ranged from less than 0.05 to 13 ppbC. Levels of α-pinene ranged from less than 0.05 to 9 ppbC. These levels are low and typical of measurements made by other investigators (8). Cronn and Harsch (12) report concentrations of isoprene ranging from non-detectable to 17.4 ppbC with a median value of 5.0 ppbC. Their α-pinene concentrations ranged from 1.2 to 8.7 ppbC with a median of 2.3 ppbC. Arnts and Meeks' (10) concentrations of isoprene ranged from nondetectable to 5.7 ppbC; the median was 3.9 ppbC. They report upper limit values for α-pinene because of interference with p-xylene. Our isoprene concentrations in the Boone samples were higher than in the remote samples. The Boone outskirts values ranged from 3.2 to 13.3 ppbC and the Boone center samples ranged from 2.6 to 8.7 ppbC. These results are probably distorted, because all of the Boone samples were collected on warm afternoons in the summer or early fall when emissions are expected to be highest.

Time series plots of temperature; sum of paraffins, olefins, and aromatics; acetylene; isoprene; α-pinene; and sum of unknowns are shown in Figures 1 and 2 to demonstrate the presence or absence of seasonal variability. Acetylene and the sum of paraffins, olefins, and aromatics show no seasonal variation. The similarity of the two plots suggest that acetylene and the paraffins, olefins, and aromatics are from the same source, primarily automobile exhaust and other anthropogenic sources. The plots indicate that typical rural concentrations of acetylene range from 0.2 to 2 ppbC and that typical sum of paraffins, olefins, and aromatics range from 20 to 40 ppbC. These plots are in contrast to the plots of temperature, isoprene, α-pinene, and sum of unknowns versus time.

The isoprene and α-pinene time series plots (Figure 2) show the expected seasonal variability, isoprene being the most distinctive. Comparison of these plots to the sampling temperatures plot (Figure 1) confirms the effect of temperature on vegetative emissions demonstrated by the growth chamber experiments of Tingey (18). For the 20 individual analyses with complete data, the percent biogenic (isoprene + α-pinene) ranged from 0 to 7.9%, and the percentages also showed a seasonal/temperature effect similar to absolute concentration variation.

The unknown hydrocarbons also show a seasonal effect (Figure 2) although not as pronounced as that of isoprene. This seasonal effect suggests that some biogenic compounds are present in the unknowns component, which is not surprising since most of the unknown peaks eluted in the region of the chromatogram where the C-10 terpenes elute, and many of the samples were collected very close to areas of dense vegetation. This effect was especially apparent for the Linville Gorge where many of the highest sum of unknowns concentrations were observed. The gorge is deep, with dense vegetation, and less atmospheric mixing than on mountain tops such as Roan Mountain or Rich Mountain. Also the absolute and relative concentrations of isoprene and α-pinene were highest in the Linville Gorge.

Conclusions

Typical ambient air concentrations of hydrocarbons in remote areas of western North Carolina were quite low. NMTHC was usually less than

100 ppbC. Identified paraffins, olefins, aromatics, and acetylene were probably anthropogenic in origin and their sum was usually less than 40 ppbC. The unidentified hydrocarbons were the largest portion of NMTHC, 45 to 59%, in the remote areas. The unidentified component of NMTHC was composed of anthropogenic and biogenic hydrocarbons. Isoprene and α-pinene concentrations were low and their sum in all cases represented less than 10% of NMTHC. The biogenic hydrocarbons displayed a distinctive seasonal/temperature variation as a function of time of year.

Appendix: Summary of Hydrocarbon Data

Table IA gives a statistical summary of the hydrocarbon composition at each of the seven locations sampled during the study. The median, minimum, and maximum concentrations are reported in ppbC for 46 individual hydrocarbons or groups of hydrocarbons. The hydrocarbons listed are ones commonly observed in urban and suburban ambient air plus isoprene and α-pinene. The median is used because it is a more efficient measure of central tendency for small numbers of observations (15).

References

1. F. W. Went, "Blue hazes in the atmosphere," Nature 187:641 (1960).

2. F. W. Went, "Organic matter in the atmosphere, and its possible relation to petroleum formation," Proc. Natl. Acad. Sci. U.S.A. 46:212 (1960).

3. R. A. Rasmussen, "Volatile organic material of plant origin in the atmosphere," Proc. Natl. Acad. Sci. U.S.A. 53:215 (1965).

4. P. E. Coffey and H. Westberg, "International conference on oxidants, 1976: Analysis of evidence and viewpoints. Part IV. The issue of natural organic emissions," EPA-600/3-77-116, U.S. Environmental Protection Agency, 1977.

5. B. Dimitriades and A. P. Altshuller, "International conference on oxidant problems: Analysis of evidence/viewpoints presented." Parts I and II, J. Air Poll. Control Assoc. 27(4):299 (1977).

6. R. A. Rasmussen, "A review of the natural hydrocarbon issue," in Atmospheric Biogenic Hydrocarbons, Vol. 1. Emissions. J.J. Bufalini, R. R. Arnts, eds., Ann Arbor Science, Ann Arbor, MI, 1981.

7. T. E. Graedel, "Terpenoids in the atmosphere," Rev. Geophys. Space Phys., 17:937 (1979).

8. A. P. Altshuller, "Review: Natural volatile organic substances and their effect on air quality in the United States," Atmos. Environ. 17(11):2131 (1983).

9. P. R. Zimmerman, "Testing of hydrocarbon emissions from vegetation, leaf litter, and aquatic surfaces, and development of a methodology for compiling biogenic emission inventories," EPA-450/4-79-004, U.S. Environmental Protection Agency, 1979.

10. R. R. Arnts and S. A. Meeks, "Biogenic hydrocarbon contribution to the ambient air of selected areas," Atmos. Environ. 15(9): 1643 (1981).

11. M. A. Ferman, "Rural nonmethane hydrocarbon concentration and composition," in Atmospheric Biogenic Hydrocarbons, Vol. 2. Ambient Concentrations and Atmospheric Chemistry, J. J. Bufalini, R. R. Arnts, eds., Ann Arbor Science, Ann Arbor, MI, 1981.

12. D. R. Cronn and D. E. Harsch, "Smoky Mountain ambient halocarbon and hydrocarbon monitoring; September 21-26, 1978," U.S. EPA Contract No. R0804033-03-2, Washington State University, Pullman, WA.

13. R. L. Seila, "Non-urban hydrocarbon concentrations in ambient air north of Houston, Texas," EPA-600/3-79-010, U.S. Environmental Protection Agency, 1979.

14. P. F. Nelson and S. M. Quigley, "The m,p-xylene:ethylbenzene ratio. A technique for estimating hydrocarbon age in ambient atmospheres," Atmos. Environ. 17(3):659 (1983).

15. R. B. Dean and W. J. Dixon, "Simplified statistics for small numbers of observations," Anal. Chem. 23(4): 636 (1951).

16. W. A. Lonneman, S. L. Kopczynski, P. E. Darley, F. D. Sutterfield, "Hydrocarbon Composition of urban air pollution," Environ. Sci. Technol. 8(3): 229 (1974).

17. R. E. Stephens and F. R. Burleson, "Distribution of light hydrocarbons in ambient air," J. Air Poll. Control Assoc., 19(12):929 (1969).

18. D. T. Tingey, "The effect of environmental factors on the emission of biogenic hydrocarbons from live oak and slash pine," in Atmospheric Biogenic Hydrocarbons, Vol. 1. Emissions, J. J. Bufalini, R. R. Arnts, eds., Ann Arbor Science, Ann Arbor, MI, 1981.

19. J. Buchanan and F. Smith, "Method for the determination of nitrogen dioxide in the atmosphere (sodium arsenite procedure)," in Guidelines for Development of a Quality Assurance Program, U.S. EPA Contract No. 68-02-1234, Research Triangle Institute, Research Triangle Park, NC, 1975.

TABLE I. Summary and analysis of hydrocarbon composition at seven locations in NW North Carolina

Compound	Roan Mt.	Grandfather Mt.	Linville Gorge	Rich Mt.	Deer Park	Boone Outskirts	Boone Center
	Median concentration, ppbC/percentage composition						
Acetylene	0.8/2.0	1.0/1	0.8/1	1.0/1	1.0/1	1.8/1	5.7/1
Paraffins	12.1/30	30.6/39	22.6/27	22.5/31	24.2/36	42.4/30	200.3/46
Olefins	2.2/6	4.5/6	1.8/2	1.7/2	2.5/4	7.7/5	54.8/13
Aromatics	3.4/8	6.5/8	4.6/5	4.8/7	5.4/8	16.2/12	72.0/17
Biogenic*	0.4/1	1.1/1	4.8/5.6	1.1/2	0.5/1	9.4/7	5.7/1
Unknown	21.4/53	35.1/45	50.6/59	41.6/57	34.6/51	63.7/45	96.0/22
NMTHC	40.3/100	78.8/100	85.2/100	72.7/100	68.2/100	141.0/100	434.5/100
No. of Samples	9	6	11	10	7	4	6
X/E Ratio†	2	2	2	2	2	3.3	3.3

* Isoprene + α-pinene
† m,p-xylene:ethylbenzene ratio

TABLE IA. Hydrocarbon compositions at seven locations in northwestern North Carolina

Compounds	Roan Mountain			Grandfather Mountain		
	Median	Min.	Max.	Median	Min.	Max.
ACETYLENE	0.8	0.3	3.2	1.0	0.9	0.9
ETHANE	2.6	1.1	5.1	9.1	7.2	13.0
PROPANE	3.4	2.0	5.1	6.0	4.7	14.4
ISOBUTANE	0.7	0.1	5.1	2.3	0.8	4.2
N-BUTANE	1.1	0.2	4.0	2.5	2.1	9.9
ISOPENTANE	0.9	0.3	7.5	3.8	1.5	6.5
N-PENTANE	0.7	0.1	3.2	1.0	1.0	4.3
2,2-DIMETHYLBUTANE	0.1	0.0	0.2	0.1	0.1	0.8
CYCLOPENTANE	0.0	0.0	0.2	0.1	0.1	0.3
2,3-DIMETHYLBUTANE	0.1	0.0	0.6	0.2	0.1	0.5
2-METHYLPENTANE	0.2	0.1	2.0	0.6	0.4	1.9
3-METHYLPENTANE	0.1	0.1	1.2	0.4	0.3	1.5
N-HEXANE	0.2	0.1	0.7	0.5	0.4	2.3
METHYLCYCLOPENTANE	0.1	0.1	0.8	0.1	0.1	0.9
2,4-DIMETHYLPENTANE	0.3	0.2	0.7	0.3	0.3	0.9
2,3-DIMETHYLPENTANE	0.1	0.0	2.0	0.5	0.4	1.4
3-METHYLHEXANE	0.1	0.0	1.3	0.3	0.2	0.8
2,2,4-TRIMETHYLPENTANE	0.2	0.0	1.3	0.2	0.2	0.8
N-HEPTANE	0.1	0.0	1.2	0.2	0.2	0.9
METHYLCYCLOHEXANE	0.1	0.0	0.7	0.2	0.2	0.8
N-OCTANE	0.1	0.0	0.3	0.1	0.1	0.4
N-NONANE	0.1	0.0	0.3	0.1	0.1	0.3
OTHER PARAFFINS	0.8	0.1	4.3	2.0	0.6	3.5
ETHYLENE	1.7	1.1	3.4	3.2	1.5	4.8
PROPYLENE	0.1	0.0	0.5	0.7	0.4	1.0
ISOBUTYLENE	0.1	0.1	0.5	0.2	0.1	0.3
1,3-BUTADIENE	0.0	0.0	0.2	0.0	0.0	0.1
T-2-BUTENE	0.0	0.0	0.3	0.0	0.0	0.5
C-2-BUTENE	0.0	0.0	0.2	0.0	0.0	0.0
1-PENTENE	1.1	0.0	0.3	0.1	0.1	0.1
2-METHYL-1-BUTENE	0.1	0.0	0.4	0.1	0.0	0.2
T-2-PENTENE	0.0	0.0	0.5	0.0	0.0	0.0
C-2-PENTENE	0.0	0.0	0.3	0.0	0.0	0.0
2-METHYL-2-BUTENE	0.1	0.0	0.7	0.2	0.1	0.3
OTHER OLEFINS	0.0	0.0	0.5	0.0	0.0	0.0
BENZENE	0.9	0.4	1.8	1.3	0.7	4.2
TOLUENE	1.0	0.7	4.5	2.6	1.4	6.1
ETHYLBENZENE	0.3	0.2	1.1	0.5	0.4	1.1
M+P-XYLENE	0.6	0.4	3.2	1.0	0.9	2.1
O-XYLENE	0.3	0.1	1.4	0.4	0.3	0.9
N-PROPYLBENZENE	0.0	0.0	0.5	0.1	0.1	0.2
M-ETHYLTOLUENE	0.2	0.1	1.1	0.4	0.1	0.6
P-ETHYLTOLUENE	0.1	0.0	0.4	0.2	0.1	0.4
ISOPRENE	0.1	0.0	7.7	0.8	0.9	1.6
A-PINENE	0.3	0.1	4.5	0.3	4.1	7.0
UNKNOWNS	21.4	11.5	78.3	35.1	31.5	54.9

* All concentrations are ppb carbon

TABLE IA. (continued)

Compounds	Linville Gorge			Rich Mountain		
	Median	Min.	Max.	Median	Min.	Max.
ACETYLENE	0.8	0.4	2.5	1.0	0.5	1.6
ETHANE	6.7	3.7	7.9	6.1	4.0	8.1
PROPANE	5.6	3.1	12.8	5.6	4.5	8.6
ISOBUTANE	0.9	0.6	7.8	0.9	0.5	1.0
N-BUTANE	2.0	1.4	3.5	2.0	1.5	2.5
ISOPENTANE	1.5	1.0	4.2	1.5	0.9	2.2
N-PENTANE	1.0	0.6	2.8	1.1	0.7	1.6
2,2-DIMETHYLBUTANE	0.1	0.1	0.2	0.1	0.1	0.5
CYCLOPENTANE	0.1	0.0	0.2	0.1	0.0	0.1
2,3-DIMETHYLBUTANE	0.1	0.0	0.4	0.1	0.1	0.4
2-METHYLPENTANE	0.4	0.3	1.9	0.4	0.3	0.7
3-METHYLPENTANE	0.2	0.1	1.3	0.3	0.1	0.4
N-HEXANE	0.3	0.2	1.7	0.4	0.2	0.7
METHYLCYCLOPENTANE	0.2	0.1	1.3	0.2	0.1	0.3
2,4-DIMETHYLPENTANE	0.4	0.3	0.8	0.3	0.0	0.4
2,3-DIMETHYLPENTANE	0.3	0.1	1.3	0.3	0.2	0.4
3-METHYLHEXANE	0.1	0.1	0.6	0.2	0.1	0.5
2,2,4-TRIMETHYLPENT	0.2	0.1	0.6	0.2	0.1	0.3
N-HEPTANE	0.2	0.1	0.7	0.2	0.1	0.3
METHYLCYCLOHEXANE	0.1	0.0	0.5	0.1	0.0	0.2
N-OCTANE	0.1	0.0	0.5	0.1	0.1	0.2
N-NONANE	0.1	0.1	0.3	0.2	0.1	0.3
OTHER PARAFFINS	2.0	0.8	7.3	1.1	0.3	2.2
ETHYLENE	0.8	0.5	3.7	1.0	0.6	1.8
PROPYLENE	0.3	0.0	0.5	0.2	0.0	0.7
ISOBUTYLENE	0.2	0.1	0.6	0.2	0.1	0.4
1,3-BUTADIENE	0.1	0.0	0.4	0.0	0.0	0.3
T-2-BUTENE	0.0	0.0	0.3	0.0	0.0	0.0
C-2-BUTENE	0.0	0.0	0.4	0.0	0.0	0.1
1-PENTENE	0.1	0.0	0.2	0.1	0.0	0.1
2-METHYL-1-BUTENE	0.1	0.0	0.3	0.1	0.0	0.1
T-2-PENTENE	0.0	0.0	0.5	0.0	0.0	0.1
C-2-PENTENE	0.0	0.0	0.3	0.0	0.0	0.0
2-METHYL-2-BUTENE	0.2	0.1	0.7	0.1	0.1	0.2
OTHER OLEFINS	0.0	0.0	0.9	0.0	0.0	0.0
BENZENE	1.1	0.7	3.5	1.1	0.8	1.6
TOLUENE	1.4	1.0	0.8	1.7	1.2	2.7
ETHYLBENZENE	0.4	0.2	1.4	0.3	0.2	0.5
M+P-XYLENE	0.7	0.4	3.9	0.7	0.3	1.4
O-XYLENE	0.4	0.1	1.4	0.3	0.2	0.5
N-PROPYLBENZENE	0.2	0.1	0.4	0.1	0.1	0.3
M-ETHYLTOLUENE	0.3	0.1	0.7	0.4	0.2	0.6
P-ETHYLTOLUENE	0.1	0.0	0.2	0.2	0.1	0.2
ISOPRENE	0.50	0.0	13.4	0.1	0.0	2.1
A-PINENE	4.3	0.7	8.9	1.0	0.5	2.5
UNKNOWNS	50.6	14.3	107.8	41.6	14.5	69.4

TABLE IA. (Continued)

Compounds	Boone Center			Boone Outskirts		
	Median	Min.	Max.	Median	Min.	Max.
ACETYLENE	5.7	2.8	8.4	1.8	1.8	1.8
ETHANE	4.7	5.3	5.5	2.6	2.5	2.6
PROPANE	8.6	6.4	13.6	4.0	3.6	4.4
ISOBUTANE	6.6	3.0	10.0	1.5	1.5	1.5
N-BUTANE	33.6	14.8	47.5	5.7	4.5	7.9
ISOPENTANE	36.8	21.0	48.3	7.0	5.2	9.9
N-PENTANE	20.5	10.9	26.2	3.7	2.4	5.6
2,2-DIMETHYLBUTANE	1.1	0.7	1.5	0.3	0.2	0.4
CYCLOPENTANE	1.6	1.0	2.4	0.2	0.2	0.4
2,3-DIMETHYLBUTANE	3.1	2.2	4.8	0.7	0.6	0.7
2-METHYLPENTANE	10.9	7.8	16.1	2.1	1.5	3.2
3-METHYLPENTANE	6.5	4.7	9.9	1.2	0.9	1.6
N-HEXANE	7.5	5.8	10.6	1.5	1.4	1.9
METHYLCYCLOPENTANE	4.7	3.4	6.9	0.7	0.6	0.9
2,4-DIMETHYLPENTANE	3.4	1.5	6.5	0.7	0.5	1.0
2,3-DIMETHYLPENTANE	7.5	3.7	13.0	1.3	1.0	1.6
3-METHYLHEXANE	3.8	2.1	6.4	0.7	0.5	1.0
2,2,4-TRIMETHYLPENT	7.0	2.4	12.5	1.1	0.7	1.7
N-HEPTANE	3.5	.9	4.9	1.1	0.5	1.5
METHYLCYCLOHEXANE	3.1	1.4	4.3	1.1	0.5	1.3
N-OCTANE	1.4	0.7	2.3	0.3	0.2	0.4
N-NONANE	1.3	0.6	2.1	0.4	0.4	0.6
OTHER PARAFFINS	23.1	23.1	23.1	4.3	1.8	6.5
ETHYLENE	14.5	8.0	17.8	3.1	3.1	3.1
PROPYLENE	5.0	3.2	7.1	1.2	1.1	1.4
ISOBUTYLENE	6.5	4.2	10.3	0.8	0.6	0.9
1,3-BUTADIENE	2.0	0.3	4.4	0.1	0.1	0.2
T-2-BUTENE	3.0	1.6	4.0	0.3	0.2	0.5
C-2-BUTENE	2.1	1.1	3.2	0.3	0.2	0.4
1-PENTENE	1.4	0.9	1.9	0.2	0.1	0.3
2-METHYL-1-BUTENE	2.5	1.5	3.7	0.3	0.3	0.5
T-2-PENTENE	2.6	1.9	3.0	0.3	0.2	0.4
C-2-PENTENE	1.4	1.1	1.7	0.4	0.1	0.8
2-METHYL-2-BUTENE	3.5	2.7	4.1	0.4	0.1	0.9
OTHER OLEFINS	10.3	5.9	14.5	0.3	0.3	0.4
BENZENE	12.7	4.5	25.0	1.9	1.4	2.5
TOLUENE	23.4	8.5	37.1	6.6	4.4	9.3
ETHYLBENZENE	4.7	1.8	7.7	1.0	0.7	1.6
M+P-XYLENE	15.3	5.2	23.7	3.3	2.7	4.2
O-XYLENE	6.0	1.7	9.7	1.2	1.0	1.7
N-PROPYLBENZENE	1.7	0.6	2.6	0.5	0.2	0.7
M-ETHYLTOLUENE	5.6	2.1	8.8	1.2	1.0	1.7
P-ETHYLTOLUENE	2.6	1.0	3.9	0.5	0.3	0.7
ISOPRENE	5.3	2.6	8.7	8.1	3.2	13.3
A-PINENE	0.4	0.2	0.6	1.3	0.1	2.2
UNKNOWNS	96.0	45.4	130.0	63.7	35.7	96.7

TABLE IA. (continued)

Compounds	Deer Park Median	Min.	Max.
ACETYLENE	1.0	1.0	1.4
ETHANE	8.1	7.2	8.4
PROPANE	5.0	4.6	35.4
ISOBUTANE	1.1	0.9	1.5
N-BUTANE	2.3	2.0	2.9
ISOPENTANE	1.6	1.2	1.9
N-PENTANE	1.2	0.7	1.3
2,2-DIMETHYLBUTANE	0.2	0.1	0.2
CYCLOPENTANE	0.1	0.0	0.2
2,3-DIMETHYLBUTANE	0.1	0.1	0.3
2-METHYLPENTANE	0.5	0.3	0.8
3-METHYLPENTANE	0.3	0.2	0.8
N-HEXANE	0.5	0.2	0.7
METHYLCYCLOPENTANE	0.2	0.1	0.3
2,4-DIMETHYLPENTANE	0.4	0.3	0.4
2,3-DIMETHYLPENTANE	0.3	0.1	0.4
3-METHYLHEXANE	0.2	0.1	0.5
2,2,4-TRIMETHYLPENT	0.2	0.1	0.3
N-HEPTANE	0.2	0.1	0.3
METHYLCYCLOHEXANE	0.1	0.0	0.3
N-OCTANE	0.1	0.1	0.2
N-NONANE	0.1	0.1	0.3
OTHER PARAFFINS	1.4	1.0	2.0
ETHYLENE	1.8	1.3	3.7
PROPYLENE	0.1	0.1	0.4
ISOBUTYLENE	0.2	0.1	0.3
1,3-BUTADIENE	0.1	0.0	0.2
T-2-BUTENE	0.0	0.0	0.0
C-2-BUTENE	0.0	0.0	0.0
1-PENTENE	0.1	0.0	0.1
2-METHYL-1-BUTENE	0.1	0.0	0.1
T-2-PENTENE	0.0	0.0	0.0
C-2-PENTENE	0.0	0.0	0.0
2-METHYL-2-BUTENE	0.1	0.0	0.1
OTHER OLEFINS	0.0	0.0	0.0
BENZENE	1.4	0.9	1.7
TOLUENE	2.1	0.9	2.6
ETHYLBENZENE	0.4	0.2	0.6
M+P-XYLENE	0.7	0.4	1.0
O-XYLENE	0.4	0.2	0.5
N-PROPYLBENZENE	0.1	0.0	0.2
M-ETHYLTOLUENE	0.2	0.1	0.3
P-ETHYLTOLUENE	0.1	0.0	0.2
ISOPRENE	0.0	0.0	4.9
A-PINENE	0.5	0.1	1.9
UNKNOWNS	34.6	18.8	76.1

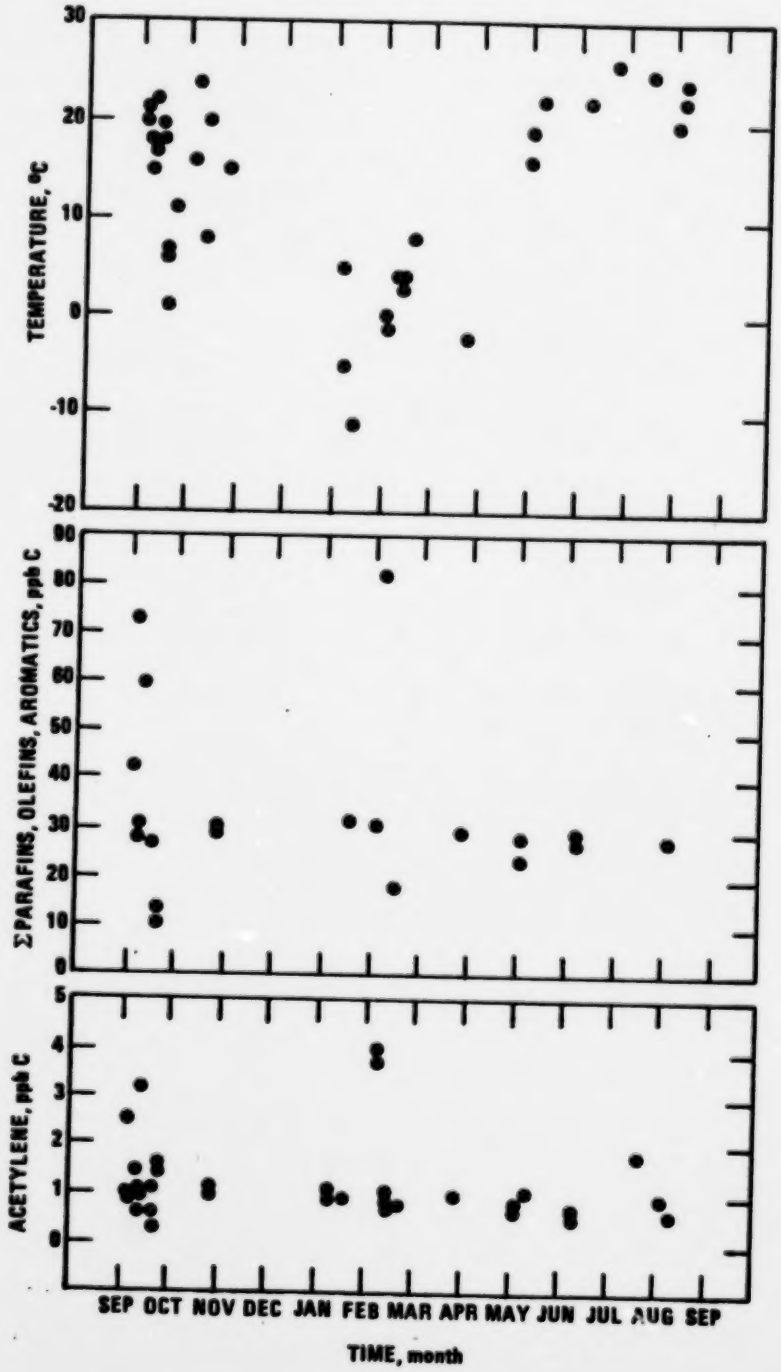


Figure 1. Seasonal variation of temperature; sum of parafins, olefins, and aromatics; and acetylene.

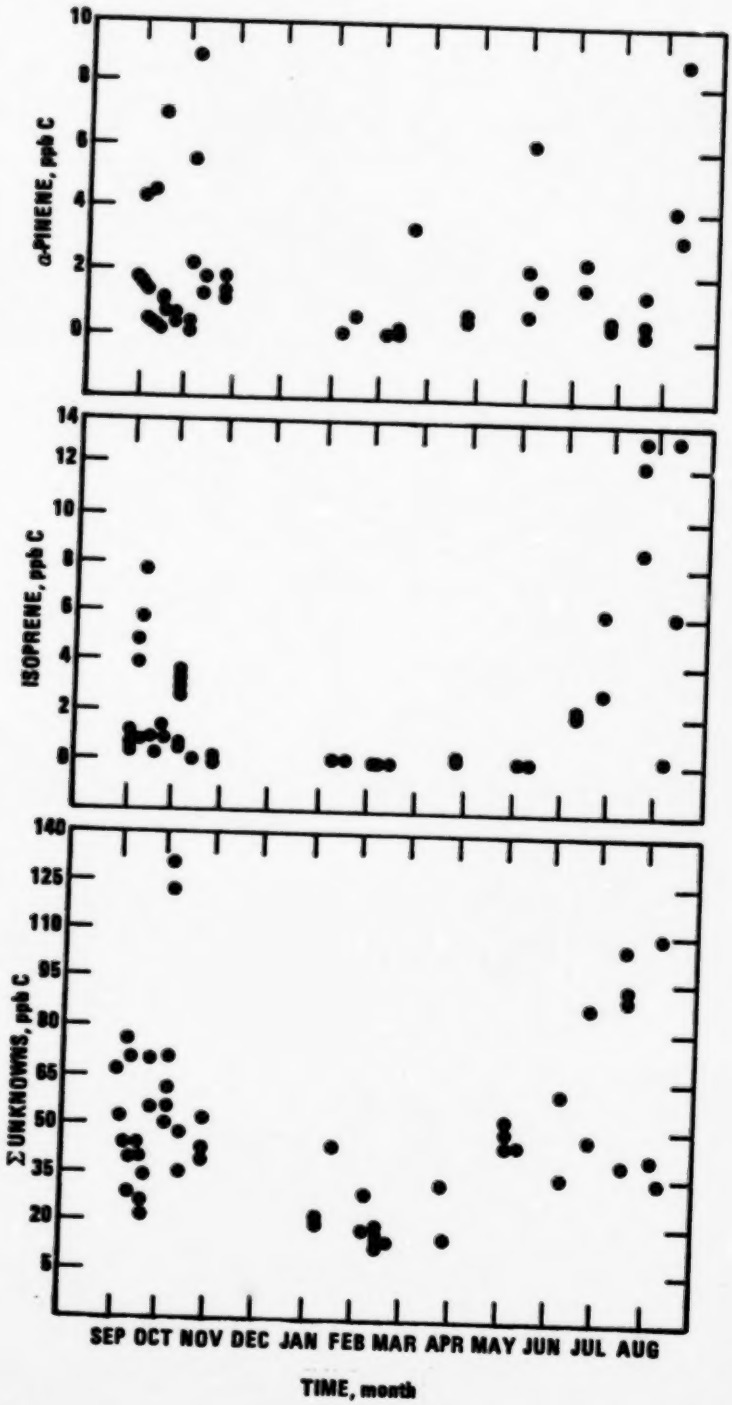


Figure 2. Seasonal variation of α-pinene, isoprene, and sum of unknown compounds.